

CALIFORNIA ENVIRONMENTAL PROTECTION AGENCY
DEPARTMENT OF TOXIC SUBSTANCES CONTROL
HAZARDOUS MATERIALS LABORATORY
ENVIRONMENTAL TECHNOLOGY CERTIFICATION PROGRAM

Technology:

**Microwave-Accelerated Reaction System, Model MARS - X, for the
Extraction of Organic Pollutants from Solid Matrices**

Manufacturer:

CEM Corporation, Matthews, North Carolina 28106-0200

Contract No.99-T1902

EVALUATION REPORT

With Appendix: Certification Statement

Certificate Number 01-01-035

December 2000

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FOREWORD

Effective January 1, 1994, Section 25200.1.5 of the California Health and Safety Code authorizes the State of California to certify the performance of environmental technologies that offer an environmental benefit. The term "technology" in this certification program designates a system, which consists of equipment, material, operating knowledge and skills, and quality control/quality assurance program on the part of both the technology vendor and the user. As part of this program, the State Department of Toxic Substances Control has evaluated the CEM microwave accelerated reaction system for the extraction of organic pollutants from environmental solid matrices. CEM is a registered trademark of CEM Corporation with U.S. patents. CEM Corporation has also acquired a license from the Government of Canada to allow customers of CEM microwave extraction instruments to use the microwave-assisted process (MAPTM) for extraction. The MAP technology and the MAP trademark are the property of the Government of Canada.

The technology is evaluated according to the guidelines for the evaluation of sample preparation methods as described in "Performance-Based Certification of Hazardous Waste Measurement and Monitoring Technologies," a California Environmental Protection Agency guidance document (www.dtsc.ca.gov/sppt/pppt/td/techcert.html).

This report is prepared to show the results of an evaluation on technology's performance. The evaluation is based on a review of validation data submitted by the technology proponent, CEM Corporation, and on specified validations by an independent party, Midwest Research Institute (MRI), whose findings the evaluation team considered reliable.

INTRODUCTION

Conventional techniques for environmental sample preparation for organic pollutants, such as extractions by shakers and separatory funnels, manual and automated Soxhlet extraction (SW-846 Methods 3540C and 3541), are time-consuming and generate large volumes of waste solvents. In consideration of the slow extraction process and the potential exposure of laboratory workers to toxic organic solvents, the development of new technologies to improve economic and environmental conditions has been driven by the regulatory agencies and the public. For this purpose, several innovative technologies have been developed during the last decade as alternatives to conventional solvent extraction.

These include ultrasonic extraction (SW-846 Method 3550B), Supercritical Fluid Extraction (SFE, Methods 3560 and 3561), Pressurized Fluid Extraction (PFS, Method 3545) for solid matrices, and Solid Phase Extraction (SPE, Method 3535) for aqueous matrices. These extraction methods use relatively less solvent with an extraction time of 10 to 30 minutes or less. Closed-vessel microwave heating technology has been used for many years for the acid digestion of samples for metal analysis. This technology has been extended to the solvent extraction of organics from solid matrices. Recently a microwave system for organic extraction became commercially available. Microwave extraction is one of the "green methods" to be approved by the U.S. EPA SW-846 Organic Methods Workgroup for incorporation into SW-846 Manual as Method 3546.²⁰

CEM's Microwave-Accelerated Reaction System (MARS) is an innovation for solvent extraction of environmental pollutants from solid matrices. It is the process of heating solid sample-solvent mixtures with microwave energy in a closed system and the subsequent partitioning of compounds from the sample to the solvent.²² The MARS has the capability to

perform both acid digestion for inorganic analysis (MARS5, digestion mode) and solvent extraction for organic analysis (MARS-X, extraction mode). For the purpose of this certification, the evaluation is limited to its performance for solvent extraction applications for organic analysis to verify performance according to the claims advanced by the CEM Corporation.

Performance Claims by CEM:

1. CEM Model MARS-X can extract a batch of up to 14 samples simultaneously per heating cycle with sample extraction times of 15 to 20 minutes.
2. The system uses microwave energy to heat the sample - solvent mixtures contained in sealed vessels rapidly to a temperature above the atmospheric boiling point of the extracting solvent.
3. The technology is used to extract environmental pollutants from solid matrices, typically soils, sediments, or sludge.
4. The technology extraction efficiency is comparable to Soxhlet extraction with an 80 to 90 percent reduction in solvent consumption and a 95 percent reduction in extraction time on a per-sample basis.
5. The maximum operating conditions for the system are 200°C and 200 psi for GreenChem™ extraction vessels; 140 psi for CleanChem™ Extraction vessels. Typical operating conditions for the extraction process are 110 to 135°C and 100 psi.
6. Samples are limited to a maximum size of 20 grams with typical sample size of 5 to 10 grams. Solvent volumes are limited to 65 mL with a typical volume of 25 to 30 mL.

SUMMARY OF PRINCIPLE OF OPERATION

Microwave energy is a non-ionizing radiation that causes heating by migration of ions and rotation of molecules with dipole moments, but by itself does not cause changes in molecular structure. It has a frequency range of 300 to 300,000 MHz with three frequencies used for industrial and scientific purposes, the most common being 2450 MHz. This frequency is used in the CEM microwave-accelerated solvent extraction system, Model MARS-X⁹. During the extraction process, dipole rotation refers to the alignment of polar solvent-sample molecules due to exposure to the electric component of the microwave field.

As the electric field decreases, induced disorder is restored which results in thermal energy being released. The ability of material to convert microwave energy into thermal energy is dependent upon its polarizability and absorption (loss factor) characteristics. The technology combines the speed of microwave heating and a closed vessel system to achieve elevated temperatures under controlled conditions. When sample-solvent mixtures in sealed vessels are exposed to microwave energy, they can achieve temperatures significantly above the atmospheric boiling point of the solvent. Consequently, the analyte desorption rate from the sample is significantly increased. For every 10°C increase in temperature there is a two-fold increase in kinetics. Unlike conductive heating, microwave heating is sample-dependent. The microwave extraction process is less dependent upon solvent affinity because of the free migration of the components toward the solvent. This often provides wider options for solvent selection for microwave extraction. This is the result of selective application of energy directly into the matrix² and the combined effect of high temperature and rapid heating of the extracting solvent in a closed-vessel system. As a result, extraction efficiency is increased and extraction time is greatly reduced.

BRIEF DESCRIPTION OF THE TECHNOLOGY

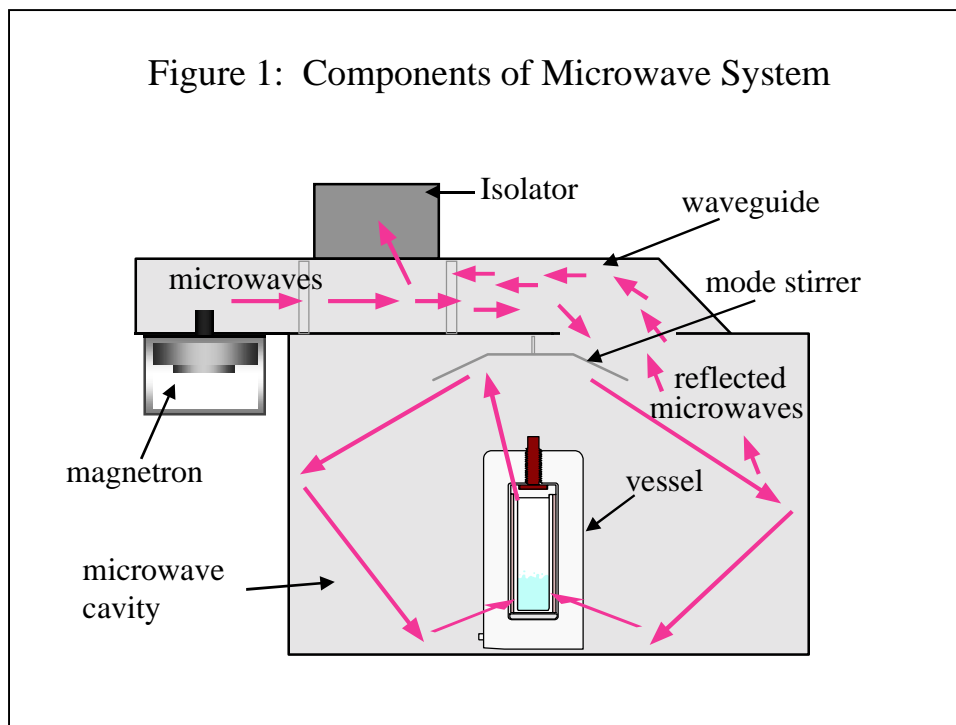
The Microwave-Accelerated Reaction System, Model MARS-X, is designed for laboratory use in extracting, dissolving, hydrolyzing, or drying a wide range of organic materials. It is a rapid sample preparation technology for a variety of analytical methods, such as GC, GC/MS, LC, etc. The extraction is performed in a closed-vessel microwave heating system under temperature and pressure controlled conditions. CEM manufactures two models of microwave extraction systems, MES-1000 and MARS-X, that have been widely used in the analytical community. The Model MES-1000 was the initial product. The advanced model, MARS-X, was released in December of 1998 and is the successor to the MES-1000. Several improvements have been made in instrumental design to enhance the structural durability, safety features, robustness of operation, and the extraction efficiency. Both

the MES-1000 and MARS-X are based on the same basic operating principle that combines the speed of microwave heating and closed (sealed) vessel technology to achieve elevated temperatures under controlled conditions. This design accelerates the migration of analytes from the solid to the solvent for subsequent analysis. The system is equipped with an inboard pressure and temperature control system for regulating sample extraction conditions via magnetron power output control.⁴

Microwave Instrumentation

The MARS-X has a microwave power system with selectable output of 0 to 1500 watts \pm 5% (IEC 705 Method-1988). The major components of the microwave system are presented in Figure 1. These include the magnetron, isolator, waveguide, cavity, and mode stirrer. Microwave energy is generated

Figure 1: Components of Microwave System



by the magnetron, propagated down the waveguide, and introduced into the cavity. The mode stirrer distributes the energy in various directions, and the cavity acts as containment housing for the energy until it is absorbed by the sample load within the cavity. The isolator protects the magnetron from energy not absorbed by the sample load. The isolator allows energy to go from the magnetron to the cavity but will not allow it to go from the cavity back to the magnetron. This feature is desirable because a magnetron is damaged when it is exposed to this reflected energy. A turntable can be used to rotate the sample load within the cavity to ensure even energy distribution.

There are two types of instrumental design: the open-vessel and closed-vessel microwave heating systems for microwave extraction. The open-vessel system performs extraction at atmospheric conditions and temperature control is unnecessary. This approach is the microwave-assisted process which operates on an input power/time basis. The microwave-assisted process is commonly used when the solvent is nonpolar or microwave-transparent and the sample is biological or agricultural tissue that has a microwave-absorbing constituent such as water.²² The closed-vessel system performs extractions in accelerated time frames at elevated temperatures under temperature controlled conditions. However, with the recent improvements, a closed-vessel microwave system can be used for the microwave extraction without using a polar solvent system; MARS-X is an example. The following describes the major changes incorporated into the MARS-X system.

Vessel Technology

A turntable assembly within the cavity contains standard vessels and one control vessel. The control vessel in the MARS-X has a temperature probe for regulating extraction conditions. Two types of extraction vessels are available for the MARS-X Model:

the GreenChem™ Extraction Vessels and the CleanChem™ Extraction Vessels. The extraction vessels have been improved from the screw-cap design to a framed design in the MARS-X Model. This makes the vessels easier to assemble and more compact. The MARS-X allows 14 samples to be processed versus 12 samples of the MES-1000.^{22, 25, 33}

GreenChem™ Extraction Vessels, with either glass or PFA Teflon liners, are designed to remain completely sealed during operation to prevent solvent and analyte loss. The inert PFA vessel liners provide no active site for compound breakdown at elevated temperatures and pressures.¹¹ All the materials used in the vessels' construction are transparent to microwaves so that the solvent-sample mixtures absorb the maximum amount of incident microwave energy, with a maximum control pressure at 200 psi and a maximum control temperature at 200°C. These vessels are designed for routine solvent extractions. The setup permits simultaneous processing of up to 14 samples containing one control vessel and 13 standard vessels per heating cycle. Specifications and instructions for the use of the GreenChem™ Vessel Set are described in the manual.^{28, 33}

CleanChem™ Extraction Vessels are made of PFA Teflon and are designed for extraction applications using aggressive solvents, such as methylene chloride or toluene. The vessel remains completely sealed up to temperatures of 200°C and pressures of 140 psi when heating organic solvents. The capacity is 12 vessels, one control vessel and 11 standard vessels.

Temperature Control Capabilities

Temperature control is necessary to optimize the extraction efficiency, prevent thermal degradation of the target analytes and to provide reproducible operating conditions. This is achieved with a temperature measurement system that is microwave

transparent so it does not cause any self-heating. The temperature probe is inserted directly into the control vessel to measure the temperature of the solvent-sample mixture. It is then used in a feedback control loop to regulate the microwave power output to achieve and maintain the operator selected extraction temperature conditions (Figure 2).

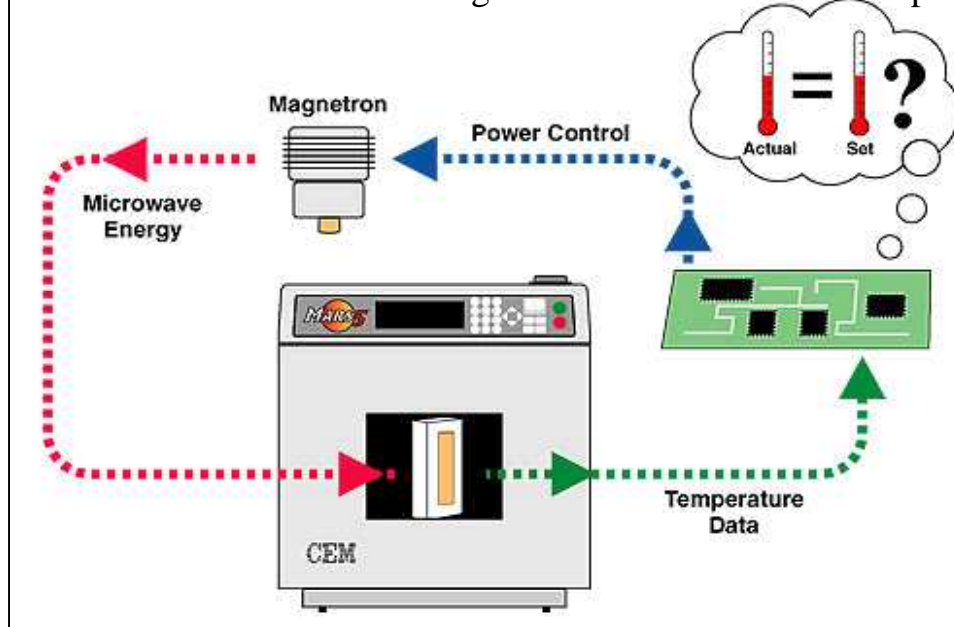
The analyst can program any temperature that is necessary for optimum extraction efficiency.³

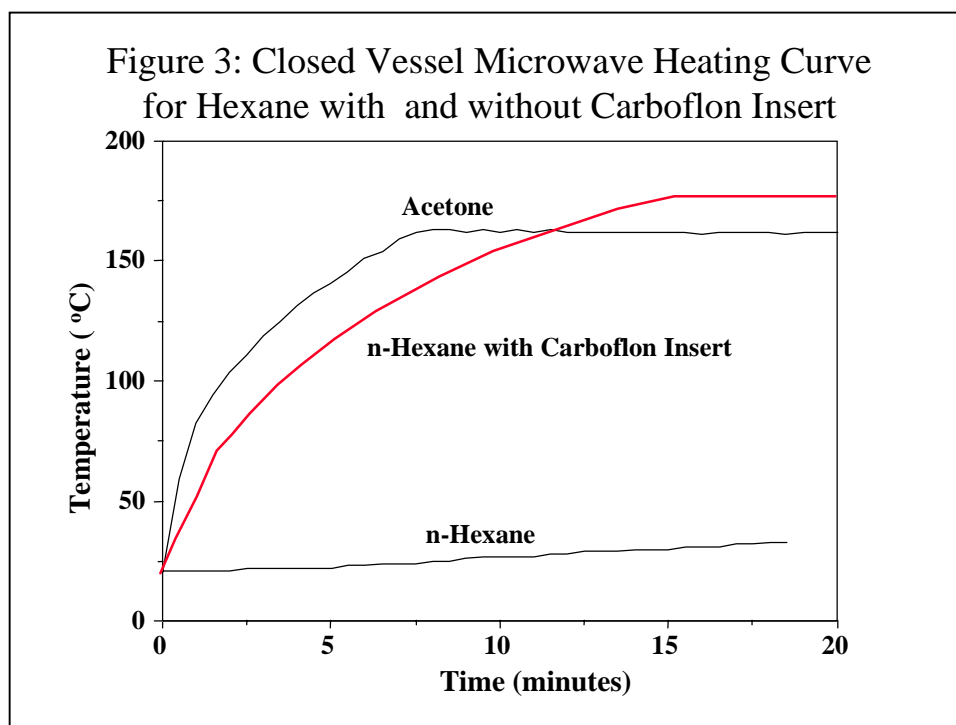
CEM also provides a safety device for measurement of the temperature in each vessel of the system. A specially engineered infrared sensor, the TempGuard™ sensor located underneath the cavity floor, monitors the temperature in each vessel as it passes the sensor. This readout is continuously calibrated to the control vessel to ensure accuracy. If the temperature in any vessel surpasses a user-defined value, the system will shut off and provide a message on the instrument screen.

Carboflon® Heating Insert

A Carboflon® heating insert provides supplementary heating for applications using nonpolar solvents in the MARS-X. The insert is a chemically inert fluoropolymer filled with carbon black, a strong microwave absorber. This insert absorbs microwave energy and transfers its generated thermal energy to the nonpolar solvent to allow heating without a change to the existing solvent scheme.²⁵ This insert is placed into the vessel with the solvent-sample mixture. Figure 3 illustrates this performance characteristic, displaying heating curves for a nonpolar solvent with and without a Carboflon heating insert. The heating curve of a polar solvent without the heating insert is used as a benchmark. Therefore, the improved model MARS-X has the potential to be a direct replacement for the conventional Soxhlet extraction technique for solid samples without a change in the solvent system.

Figure 2: Schematic of MARS Thermo-Optic Temperature Feedback Control to Regulate Microwave Power Output





Stirring

Stirring increases the surface area contact between the sample and solvent. This offers the benefit of improved extraction efficiency and decreased solvent consumption. Stirring is achieved in the MARS-X with the use of a rotating magnet below the cavity floor and the placement of a magnetic spinbar in the extraction vessel. The magnet creates a rotating magnetic field that couples with the spinbar in the vessel to create a stirring effect. The spinbars are either coated with an unfilled fluoropolymer for applications using polar solvents or a carbon black filled fluoropolymer for applications with nonpolar solvents.

External Computer Control

An external software package allows programming and operation of the MARS-X from an external computer. The package also provides electronic data (temperature versus time for the extraction process) collection and report writing capabilities.

With these improvements, the MARS-X allows an increase in sample throughput, better control of temperature, better extraction

efficiency, and easy operation. The MARS-X Operation Manual provides instructions for instrument installation, system setup and calibration, and method parameters created for the extraction of various types of analyses and matrices.²⁶ A workstation for the operation of MARS for organic extraction includes a filtration system (syringe filtration kit and Vacuum Filtration system, VAF-100TM), Vacuum Assisted Concentration/Drying Accessory (MicroVapTM), Nitrogen Evaporator, and CEM extraction vessels.³³

MATERIALS AVAILABLE FOR EVALUATION

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 31. Standard practice for solvent extraction of total petroleum hydrocarbons from soil and sediments using closed vessel microwave heating. ASTM Designation: D 5765 - 95, 1-3.
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**TECHNICAL EVALUATION:
GENERAL CONSIDERATIONS**

The reproducible and effective recovery of target analytes from the matrix is a basic requirement for a valid sample extraction technology. Reproducible extraction requires the use of an appropriate solvent, adequate sample dispersion, and sufficient time for partitioning analytes from the soil or other solid matrices. Important aspects for the

evaluation of a sample extraction technique are: (1) the recovery of target analytes from the matrices of concern under the established conditions; (2) the time and solvent required for the extraction; (3) the applicability of the technology to a wide variety of the specified sample matrix or matrices; and (4) the stability of the chemicals under the specified extraction conditions. On the basis of the data packages submitted by the technology developer/manufacturer and the available literature, the technology was evaluated with regard to the following aspects:

1. **Operating Parameters:** standard operating conditions and parameters that affect the extraction efficiency and recovery of target analytes, and conditions for specific applications;
2. **Recovery Data and Matrix Effects:** the accuracy and precision of analyte recovery from various matrices, and the extraction efficiency of specified chemicals or classes of chemicals;
3. **Comparability:** comparisons of performance with other established sample extraction techniques with respect to recovery data, extraction efficiency, economic, and environmental benefits;
4. **Quality Control and Quality Assurance Program:** instructions for instrument calibration and routine maintenance and procedures followed by the user to assure the data quality;
5. **Manufacturability:** the quality control in the manufacturing process, including the materials for construction, the instrument assembly; safety features, and consistency in functional characteristics and reliability;
6. **Health and Safety:** general guidelines for safety operation of laboratory microwave systems, Materials Safety Data Sheet (MSDS), operators' training, and

instructions for general environmental safety.

TECHNICAL EVALUATION: CONSIDERATIONS SPECIFIC TO THIS PRODUCT

As part of the research program, the U.S. EPA Environmental Monitoring Systems Laboratory in Las Vegas evaluated innovative sample preparation techniques that could minimize pollution in analytical laboratories, while effectively extracting target analytes from an environmental medium at reduced cost. The Midwest Research Institute (MRI) in Mountain View, CA was under contract with the U.S. EPA to carry out the work investigating the microwave technology and its applicability as a tool for solvent extraction. As the CEM MARS-X has not been in the market long enough to generate sufficient data for this evaluation, the performance data and information used for this evaluation are mostly based on that generated by the earlier CEM Model MES-1000. Since both the MES-1000 and MARS-X are based on the same operating principle, with new features incorporated in the MARS-X, the MARS-X would have comparable extraction efficiency with better temperature control and easier operation at a reduced cost without sacrificing any of the performance characteristics established for the MES-1000. Information received from users with experience in working on both MES-1000 and MARS-X and the recent recovery data generated from MARS-X⁴² support this conclusion.

Operating Parameters

1. Standard Operating Procedure

For the standard operating procedure, a 5 to 10 gram portion of solid sample is weighed into the extraction vessel. Approximately 25 to 30 mL of appropriate solvent are added into the vessel. The extraction vessel is sealed and

placed in the microwave system. Extraction is performed at a temperature of 110 to 115°C at a pressure of 50 to 175 psi for 15 to 20 minutes. The applied microwave energy is regulated by the temperature feedback control mechanism of the instrument. After extraction, the vessel is allowed to cool to room temperature before it is opened to avoid loss of analytes. The supernatant is separated from fine particles by decantation, centrifugation, or filtration. The extract is then subjected to analysis using appropriate established analytical methods.

CEM conducted extensive studies to determine the optimal operating parameters of a closed-vessel microwave system.^{4,11}

extraction solvents at atmospheric pressure, the microwave energy heats samples and solvents in a closed, pressurized extraction vessel. Under this condition, the temperature can be rapidly increased above the boiling point of the solvent. Table 1 shows that the solvent temperature in the closed system at 175 psi relative to the atmospheric boiling points. One can achieve temperature increases of 100°C or more.⁷

Polar solvents with large dipole moments and dielectric constants will heat rapidly in a microwave field while nonpolar solvents are transparent to microwave energy. The solubility of an analyte can be affected by its solvating characteristics and the temperature

Table 1. Comparison of Solvent Boiling Point and Closed-vessel Temperature		
<u>Solvent</u>	<u>Boiling Point (°C)</u>	<u>Closed Vessel Temperature (°C)^a</u>
acetone	56.2 ^c	164
acetone-cyclohexane 7:3	52	160
acetonitrile	81.6 ^c	194
dichloromethane	39.8 ^c	140
hexane	64.7 ^c	162 ^b
methanol	68.7 ^c	151
^a At 175 psi		
^b Using Carboflon Heating Insert		
^c Lange's Handbook of Chemistry, 14th ed. J.D. Dean, , 1922:11.10-11.12		

Guidance for the analysis of specific analytes in various environmental matrices is published in CEM Application Notes.²⁷ These include conditions for the extraction of PAH, TPH, pesticides, and PCBs from various environmental solid matrices, such as soil, sediments. The following describes some of the important factors that may affect the technology performance.

2. Effects of Solvent and Solvent Volume

Unlike conventional extraction methods that are subject to the boiling temperature of

of extraction.³ High solvent temperatures increase extraction efficiency and thus reduce extraction time. Therefore, the selection of an appropriate solvent or solvent mixture is crucial for the migration of compounds from the sample matrix into the solvent. It has been shown that the recoveries of chlorinated pesticides were improved by changing the solvent ratio of acetone to hexane from 1:1 (v/v) to match the azeotrope's vapor phase ratio of 3:2 (v/v).¹¹ A solvent system consisting of a water-miscible solvent and water-immiscible solvent is commonly used in extraction to facilitate the extraction of wet

solids and to extract the polar analytes. Analyte solubility can be maximized by adjusting the solvent mixture and controlling the temperature.³

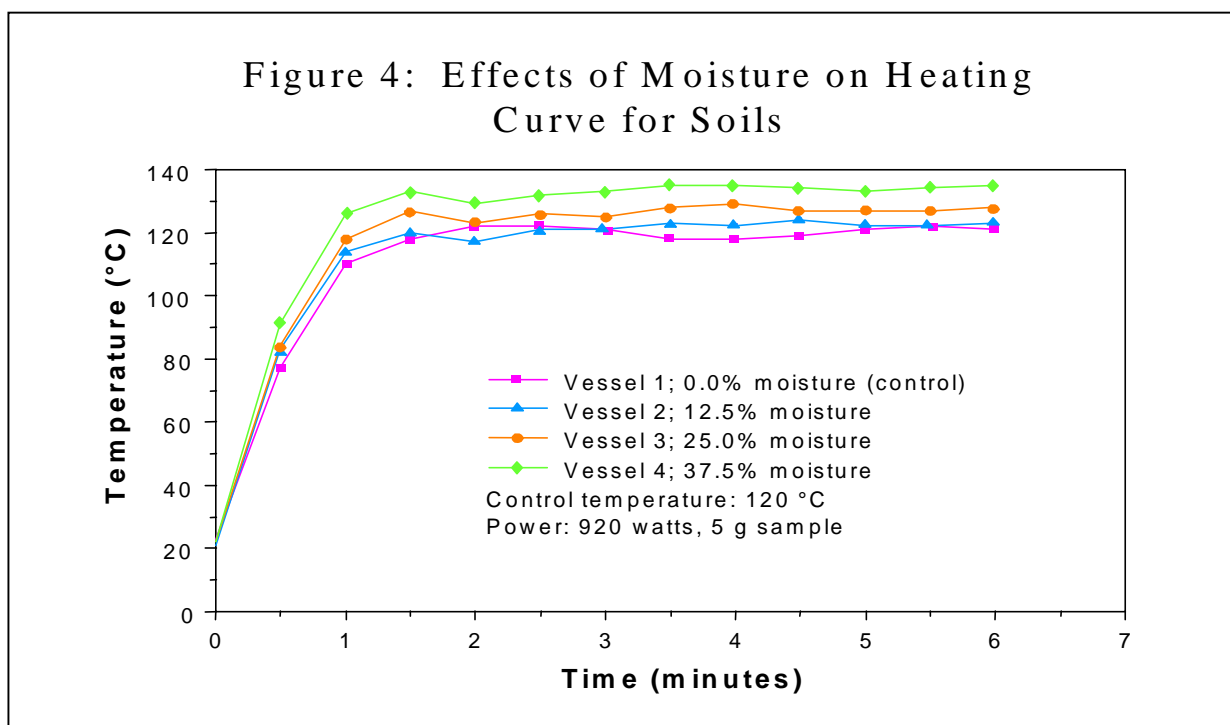
Some applications require the use of nonpolar solvents to extract the target analytes. This could present an obstacle for the use of the microwave extraction technology since the nonpolar solvent will not absorb microwave energy and heat. As indicated in the previous section, however, the user can overcome this problem by using the chemically inert Carboflon heating insert, a strong microwave absorber, to transfer the thermal energy to the solvent-sample mixture. This allows use of the microwave extraction technology with nonpolar solvents.²⁵ Results from several studies suggest that solvent systems commonly used for Soxhlet extraction can be effectively used for microwave extraction but use less solvent and less time for extraction.^{3, 4, 8, 11} Since 1:1 (v/v) acetone-hexane is widely used in the standard Soxhlet method for semivolatile organic compounds, this solvent system was most commonly selected for use in the CEM Microwave-Accelerated Solvent Extraction System to maintain method consistency. As with other sample extraction methods, however, the operating conditions

for the Microwave-Accelerated Solvent Extraction System are analyte and matrix dependent. In one case, the results indicated no difference in the recoveries of PAHs from a soil sample when using acetone instead of dichloromethane; while inconsistent results were obtained for the extraction of other soil samples using acetone.⁹

MRI evaluated the effect of solvent volume, with and without the matrix by varying the solvent volume from 5 to 30 mL.⁴ The mixed solvent, hexane-acetone (1:1), was used for this study. With a 30-mL volume the maximum temperature (156 - 160°C) can be reached within 2.5 min vs 17 min for a 5-mL volume. When various solid matrices were added, the effect of the matrix appeared to be insignificant. Typically, solvent volumes of 25 to 30 mL for a sample size of 5 to 10 g are sufficient for the extraction of chemicals listed as EPA priority pollutants.²³

3. The Effect of Moisture

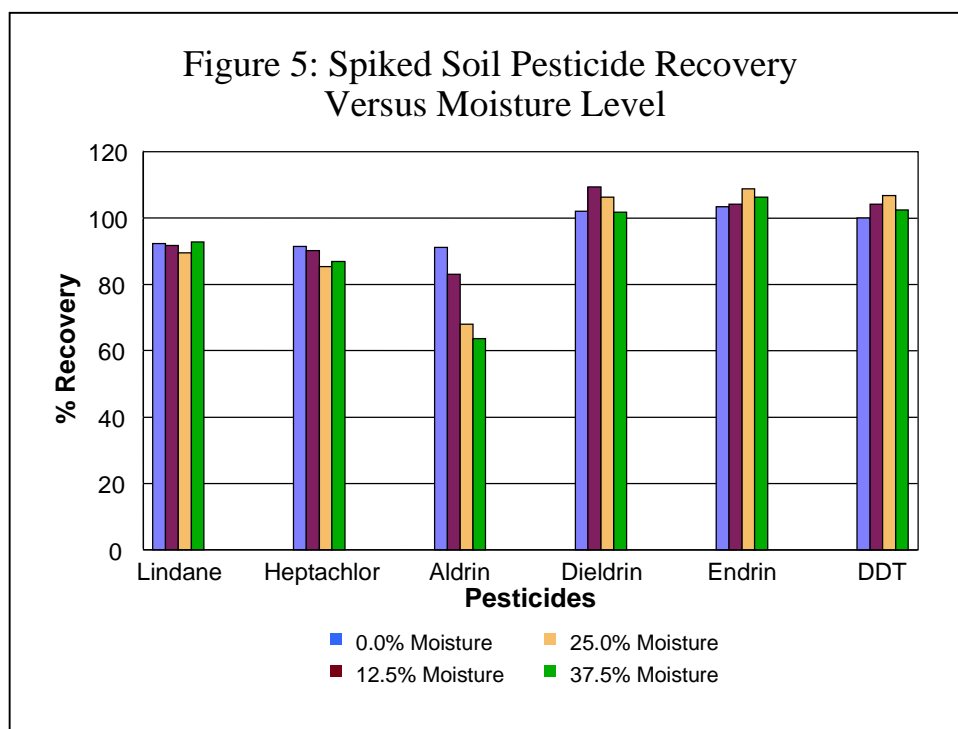
Due to the microwave absorbing properties of water, high-moisture samples would reach a higher temperature than low-moisture samples. In order to determine the ability to run multiple samples simultaneously with different



moisture contents, CEM carried out a series of studies to determine the effect of moisture content on the operating system.^{14, 41} To determine the extent of temperature variations, CEM prepared vessels with oven-dried soils to which water was added to the soils to reach moisture contents up to 37.5%. Thirty-five mL of solvent were added to each vessel. The vessels were then heated to 120°C and held for 5 min. The control vessel with no water added reached the set temperature in about 1.5 min while those containing moisture continued to heat above the set point. Depending on the solvent system used and the moisture content, the temperature varied accordingly. The maximum temperature differential relative to the dry sample was 12°C, observed for the sample containing 37.5% moisture. Figure 4 presents the heating curves for the four soil samples with 1:1 acetone-dichloromethane.¹⁴

Since the magnetron of the unit only operates when the control vessel drops below the set temperature, the control vessel should contain a matrix with the least amount of water.

To determine the effect of moisture on the recovery of chlorinated pesticides, a matrix spike mixture containing lindane, heptachlor, aldrin, dieldrin, endrin, and 4,4'-DDT was added to the above soils containing 0, 12.5, 25, and 37.5% of water. The four soil samples with varying levels of moisture were extracted within the same run. The temperature was controlled by the sample with 0% moisture added at 120°C for 20 min. The results indicated that no apparent difference in recoveries for the compounds selected (Figure 5). The poor recoveries of aldrin may be attributed to inappropriate solvent selection. The recovery of aldrin could be improved by increasing the ratio of acetone to methylene chloride to 3:2. The range of temperatures in samples containing varying moisture levels during the extraction does not affect the recoveries of these compounds under these conditions.



MRI also carried out a study to investigate the effect of moisture on the recoveries of two reference soils containing PAHs, and selected acid, base, and neutral compounds.⁴ The analyses were performed on dry and wet matrices to evaluate the effect of moisture on the microwave extraction under the established conditions (Table 2). The wet

4. Effect of Temperature, Pressure, and Extraction Time

The effect of sample extraction time and temperature on the recovery of 17 PAHs was investigated by MRI.⁴ Six standard reference materials consisting of 4 marine sediments and 2 soils were subjected to Microwave-

Table 2. Average Recoveries and Percentage RSDs for ERA Soil				
Compounds	(mg/kg)	EPA method ^a Recovery (ave.%)	MAE	
			Recovery (ave.%)	RSD (%,n=6)
<i>Native Compounds</i>				
anthracene	7.2	63	73	11
benzo(a)anthracene	5.2	66	74	10
benzo(k)floranthene	2.4	63	49	8.6
chrysene	9.5	64	85	11
naphthalene	7.8	59	60	13
pyrene	6.3	66	75	10
dibenzofuran	6.5	74	81	9
1,2-dichlorobenzene	13	44	39	18
1,3-dichlorobenzene	8.6	31	26	16
1,2,4-trichlorobenzene	1.9	57	59	13
2,4-dinitrotoluene	4.8	80	106	14
bis(2-ethylhexyl)phthalate	1.5	90	75	10
isophorone	4.7	67	77	12
4-chloropphenyl phenyl ether	3.4	81	79	9.3
butylbenzy phthalate	8.5	74	90	12
Phenol	3.9	65	72	19
2-methylphenol	3.4	47	35	15
3-methylphenol	4.6	65	72	14
2,4,6-trinitrophenol	9.4	57	89	14
pentachlorophenyl	9.6	43	65	39
<i>Spikes</i>				
anthracene-d10	5.6		83	12
fluoranthene-d10	5.6		83	9
benz(a)anthracene-d12	5.6		85	9
^a typical recoveries of approved EPA method reported by ERA				
Data presented is part of Table 5 in Anal.Chem.1994, 66, 1097-1106.				

matrix contained 20% water. Percent recoveries of these compounds relative to the certified values were all close to 80% and did not appear to be affected by the moisture present in the sample. The results of this study are consistent with the finding of CEM.

Assisted Extraction (MAE) with hexane/acetone (1:1) at ambient temperature as well as at 80, 115 and 145°C after reaching the set temperature for 5, 10, or 20 min. At the 95% confidence interval as a function of temperature across the 17 compounds and six

matrices, the average recoveries indicated that the recovery at ambient temperature (52%) was significantly lower than that obtained at 80, 115, and 145°C (70%, 75.5% and 75%, respectively). However, no significant differences in recovery were observed at 115 and 145°C. The average recovery increased slightly with extraction time but this difference was not statistically significant. A 5-min extraction at 115°C was sufficient to extract PAHs from soil or sediment matrices.

The recovery data for soil and sediment samples containing base/neutral and acidic compounds showed the same trend as in the results of PAHs. Recovery at 115°C was significantly higher than at room temperature. Pressure is another variable affecting the extraction efficiency but is directly controlled by the temperature of a particular solvent in a closed system. The effect of pressure was not evaluated independently.⁹

These experimental results support the claim that typical operating conditions for the extraction process are 110 to 135°C at 100 psi.

Extraction times are 15 to 20 minutes for a batch of up to 14 samples.²³ The instrument calibrations for microwave power, solvent sensor, temperature and pressure as they pertain to the operation of MARS-X are described in the operating manual.²⁶

Recovery Data and Matrix Effect

To evaluate method performance, the extracts obtained from microwave extraction using MES-1000 were analyzed using SW-846 method 8270A for semivolatile compounds, Method 8080 for organochlorine compounds, Method 8141 for organophosphorus pesticides (OPP), and Method 8150A for chlorinated acid herbicides. The following presents some of the recovery data and precision data of microwave extraction using the MES-1000.

1. Recovery and Precision

1.1 PAHs

To evaluate the method precision and accuracy, MRI extracted five to six 5-g portions of the standard reference soils under the established conditions.⁴ One certified standard reference soil was natural material contaminated with 14 PAHs, dibenzofuran, and pentachlorophenol with concentrations ranging from 16 to 1450 mg/kg. The percent recoveries relative to the certified values were greater than 80% with RSDs mostly within 5% (n=6), except naphthalene (11.7%) and pentachlorophenol (14.3%). The other standard reference material (ERA soil Lot No. 323) contained 20 compounds with their certified values as indicated in Table 2. The recoveries obtained by MAE were comparable to those obtained with the EPA-approved methodologies. There was more spread in the average recoveries, because the soil contained compounds with a wider range of volatilities than other reference soils.

1.2 Chlorinated Pesticides

Previous studies indicated that chlorinated pesticides could be effectively extracted by MAE.³² Forty-five chlorinated pesticides listed in Method 8081 were spiked into topsoil. The freshly spiked topsoil was extracted by microwave solvent extraction using the MES-1000 under the established conditions. The spiking levels ranged from 20-200 µg/kg. Ninety five percent of these compound recoveries were greater than 77% (after correction for analyte loss during blow down evaporation of solvent). The RSDs were mostly less than 5% (n=3), with the exception of 4 compounds (DBCP, etridiazole, hexachloropentadiene, and t-permethrin) having RSDs greater than 10%. The recoveries of some chlorinated pesticides of common interest can be found in Table 3 of ASTM D 6010-96.³²

Significantly lower recoveries of native

compounds relative to the spiked matrix, however, had been observed in several studies, and a common downward trend was observed in the recoveries of spiked and aged soil relative to freshly spiked soil samples.^{4, 8}

There was more spread and decreasing recoveries for semivolatile organics and chlorinated pesticides as the soil aged from 24 hr to 14 days or 21 days.⁸ The organophosphorus pesticides appeared not to be affected as much. Whether the loss of target compounds was due to microbial degradation or other chemical transformations warrants further investigations.

1.3 Polychlorinated Biphenyls (PCBs)

Studies on the recoveries of polychlorinated biphenyls (PCBs) from MAE were carried out on 4 soils collected from a Superfund site and a set of QC samples containing Aroclor 1060, 1254, and 1260.⁸ The QC samples were 5

(n = 4). The recoveries of 4 soils collected from a Superfund site containing Aroclor 1248 ranged from 75 to 157%. As shown in Table 3, the sample with an RSD of 35% had very low concentration (0.033 mg/kg). For Superfund samples at such a low level, a large measurement error is to be expected.

The effects of soil types on the recoveries of PCBs were also investigated. Aroclors 1016 and 1260 were spiked at two concentrations at 100 and 500 ng/g into three different soil types (clay, topsoil, and sand) and subjected to MAE. The results indicated that the average recoveries were greater than 70% for both Aroclor 1016 and 1260 from all three soil types, except for Aroclor 1260 recovery from clay soil at 62%. The RSDs (n=3) obtained from three matrices were all less than 7%, with the exception of 17% for Aroclor 1016 extracted from topsoil.⁵ The extraction efficiencies and precision of selected PCB

Table 3. MAE Method Performance of PCBs

Matrix	certified value (mg/kg)	Aroclor type	Recovery ^a (ave.%)	RSD (%,n=4)
HS-1 marine sediment	0.022	1254	93	8.1
HS-2 marine sediment	0.112	1254	77	6
ERA soil	394	1260	83	2.6
freshly spiked topsoil	0.1	1016	74	5.6
		1260	76	4.2
spiked topsoil aged for 24 hr at 4C	0.1	1016	80	14
		1260	82	10
Superfund site soil 1	465	1248	102	3.5
Superfund site soil 2	1.13	1248	157	6.3
Superfund site soil 3	0.033	1248	87	35
Superfund site soil 4	6.7	1248	75	17
^a Recoveries were not corrected for losses during blowdown evaporation				
Data presented is part of Table 3 in Anal.Chem.1995, 67, 2096-2102.				

certified reference materials (2 marine sediments, ERA soil, freshly spiked topsoil and a spiked and aged topsoil). As indicated in Table 3, the recoveries of reference samples ranged from 74 to 93% (uncorrected for blowdown evaporation) with RSDs less than 10%

congeners (CB-101, CB-118, CB-135, and CB-180) were also investigated.⁴⁰ The precision was good. In five determinations, the %RSDs were all less than 10% for every congener.

1.4 Acid, Base, and Neutral Compounds

There are 92 compounds listed in EPA Method 8270 for acid, base, and neutral compounds. With the exception of benzo(b)fluoranthene, benzo(k)fluoranthene, and n-nitrosodimethylamine (due to technical difficulty), a mixture of 89 compounds was spiked into topsoil.⁸ The spiking level was 5 mg/kg for each compound. The spiked samples were extracted by microwave heating under the established standard operating procedures.

The recoveries of these compounds can be found in ASTM, Designation: Table 1, D 6010 – 96.³² The recoveries of 79 compounds from freshly spiked soil ranged from 80 to 120%; the recoveries of 14 compounds were below 80% in which 5 compounds were below 20%. These 5 compounds are benidine, α,α -dimethylphenethylamine, 2-picoline, dibenzo-(a,j)acridine, and 2,4-dinitrophenol. These compounds generally present analytical problems in recovery.^{4,8} In 4 replicate analyses, the RSDs for the freshly spiked topsoil were below 10% for 64 of the 95 compounds, 10-20% for 25 compounds, and 28-39% for four compounds.⁸ Overall, the microwave extraction technique performed adequately for the semivolatile compounds listed in Method 8270C. Table 5 presents one of these studies on the recoveries and precision of this group of compounds.¹² As indicated, the recoveries were all within EPA QC criteria, with the exception of three chlorobenzenes as discussed below (see Comparability Section for Acid, Base, and Neutral Compounds).

1.5 Organophorus Pesticides (OPPs)

Forty-seven of OPPs listed in EPA Method 8141A were spiked into soil for the study. The recoveries of these compounds can be found in ASTM, Designation: Table 4, D 6010 – 96.³² Carbophenothion, diazinon, parathion methyl, and terbufos were not included because of the analytical difficulties

in GC analysis. Forty-one out of 47 OPPs had recoveries between 50 -120%. Six compounds, monocrotophos, naled, phosphamidon, TEPP, trichlorfon, and HMPA had recoveries below 20%. Recoveries were improved to 34-98%, however, when extractions were performed from aged topsoil samples to which water (2mL) was added. The presence of water in the matrix was found to improve in recoveries from aged topsoil samples.⁸

1.6 Total Petroleum Hydrocarbons (TPHs)

For the recoveries of total petroleum hydrocarbons using microwave extraction, CEM used three soil samples contaminated with different types of petroleum hydrocarbons in different matrices.⁷ Duplicate soil samples and a solvent blank were heated in the microwave apparatus under standard conditions. As indicated in Table 10 (in the following section), the recoveries of TPHs from soils contaminated with diesel fuel and soil contaminated with high molecular weight oil were all in good agreement with the certified values from microwave extraction. Precision is excellent for microwave and Soxhlet methods, specifically for extracting the high-molecular weight components.

2. Matrix Effect

Just as in other extraction methods, the studies indicated that microwave extraction was matrix-dependent. Studies on recoveries of six certified reference materials containing 17 PAHs indicated that the average recoveries, at the 95% confidence intervals, were a function of six matrices under study. These matrices included four marine sediments (HS-3, HS-4, HS-5, and NIST1941) and two soil samples SRS103-100 and ERA soil (Lot No 323). Three HS standards are marine sediments collected from Nova Scotia. The NIST1941 is a sediment collected from Baltimore Harbor. The average recovery of PAHs from a low concentration sample (HS-4 with concentrations ranging from 0.15 to 1.25

mg/kg) is higher than a concentration sample (HS-5 with high concentrations ranging from 0.2 to 8.4 mg/kg). The NIST sediment with concentrations comparable to HS-4 marine sediment gave even higher recoveries than HS-5. The ERA soil was spiked, homogenized, and weathered materials. Recovery was 83%, almost comparable to that of the spiked sample. Therefore, it appears that the matrix effect is more significant than

analyte concentrations. The recoveries of PAHs from reference materials ranged from 65 to 85%.^{4,9}

3. Thermal Degradation

An important aspect for success in extraction was the avoidance of thermal degradation of analytes during the extraction process. It is a concern of EPA that the microwave radiation

Table 4. Compounds Investigated for Thermal Degradation	
PAHs	
acenaphthene	chrysene
acenaphthylene	fluoroanthene-d10
anthracene	fluorene
anthracene-d10	fluoranthene
benzo(a)anthracene	indeno(1,2,3-cd)pyrene
benzo(a)anthracene-d12	naphthalene
benzo(a)pyrene	Phenanthrene
benzo(b+k)fluoranthene	pyrene
benzo(ghi)perylene	
Base/Neutral Compounds	
dibenzofuran	2,4-dinitrotoluene
1,2-dichlorobenzene	4-chlorophenyl phenyl ether
1,3-dichlorobenzene	butyl benzyl phthalate
1,2,4-trichlorobenzene	isophorone
Phenols	
phenol	4-chloro-3-methylphenol
2-chlorophenol	2,4,6-trichlorophenol
2-methylphenol	2,4-dinitrophenol
3-methylphenol	4-nitrophenol
2-nitrophenol	2,3,4,5-tetrachlorophenol
2,4-dimethylphenol	2-methyl-4,6-dinitrophenol
2,4-dichlorophenol	pentachlorophenol
Organochlorine Pesticides	
a-BHC	dieldrin
b-BHC	4,4'-DDE
r-BHC	endrin
delta-BHC	endosulfan-II
heptachlor	4,4'-DDD
aldrin	endrin aldehyde
heptachlo epoxide	endosulfan sulfate
r-chlordane	4,4'-DDT
endosulfan-I	endrin ketone
a-chlordane	methoxychlor
Data presented is part of Table 1 in Anal.Chem.1994, 66:1097-1106.	

may result in degradation of the more thermolabile semivolatile compounds, such as phenols, phenoxy acid herbicides, and organophosphates during the extraction process due to solvent-analyte interactions. A joint EPA-Environment Canada study using split samples distributed among six laboratories adequately demonstrated that the microwave radiation had no detrimental effect on the recoveries of these groups of compounds.²⁰

To test for possible degradation during the extraction, MRI performed experiments to determine the thermal stability of various groups of compounds. Compounds under this investigation are listed in Table 4.⁴ In these experiments, solvent (hexane/acetone, 1:1) and soil spiked with target compounds were heated at 115°C for 10 min at 50% power. Three determinations were performed in each study.

All the recoveries of 18 PAHs from soil were above 73%, except naphthalene, 66%. The recoveries of 9 selected base/neutral compounds ranged from 62 to 97%. In consideration of possible losses during the preparation process (filtration and blowdown steps), the volatile characteristics of naphthalene and chlorinated benzene, and the measurement error, a loss of 30% is not unreasonable. Therefore, the degradation of PAHs and base/neutral compounds can be assumed to be negligible.

For 14 phenols, all recoveries ranged from 80 to 111% from spiked solvent and greater than 70% from spiked soil, with the exception of 2,4-dinitrophenol and 2-methyl-4,6-dinitrophenol with recoveries of only 9.4 and 17%. Since the recoveries of these two compounds from heating in solvent alone are 106% and 111%, these results suggested that reactions occurred in the presence of soil other than thermal degradation caused by microwave energy.

The recoveries of 20 chlorinated pesticides

from spiked solvent ranged from 83 to 117% with RSDs within 6%. The recoveries from spiked soil ranged from 74 to 123%, with the exception of methoxychlor at 169%. The RSDs ranged from 8 to 22%. No evidence of degradation for the organochlorine pesticides was observed. The spiked organochlorine pesticides did not degrade even after subjected to 20 min of microwave extraction under the conditions established.⁴ Because of the known thermal instability of endrin and DDT, the recoveries of these two compounds were investigated by CEM.¹¹ These two compounds at 4 µg each were added to 30 mL of 1:1 (v/v) acetone-hexane and heated in the microwave unit at 150°C for 15 min. Very little breakdown products of endrin or DDT were detected in this study.

The thermal degradation of PCBs was evaluated using Aroclor 1016 and 1260 which were subjected to microwave extraction under various conditions: in the presence of solvent alone, solvent with dry topsoil, and solvent with wet topsoil. These experiments were conducted at 50°C and 145°C for 5 and 20 min at 100% power (1000W). The recoveries in every case were above 71% for Aroclor 1016 and above 80% for Aroclor 1260 without correcting for blow-down losses; thus, the possibility of PCB degradation upon heating of solvent/soil suspensions with microwave energy was negligible.⁵

Comparability

Comparisons of the performance of microwave-assisted extraction with conventional extraction techniques for environmental applications have been extensively studied by MRI and other investigators.^{4,5,7, 8,9,11,12,21, 31, 32} Methods of Soxhlet, sonication, and supercritical fluid extraction (SFE) are commonly used for these comparisons. The CEM MES-1000 was the device used for the evaluation of the extraction efficiency by microwave energy. The results of some major studies are summarized in the following.

1. Semivolatile Organics

MRI conducted a study to compare the extractability of a group of semivolatile compounds under the established conditions.

In this study, freshly spiked soil samples and 2 standard reference materials were extracted with hexane-acetone (1:1) by MAE and Soxhlet extraction, with methylene-acetone (1:1) by sonication, and with supercritical carbon dioxide modified with 10% methanol

1.1 Acid, Base, and Neutral Compounds

Table 5 compares the results for the analysis of a certified ERA reference soil. The recoveries of 23 compounds known to be included in ERA soil and 6 deuterated surrogates were all within the acceptable QC criteria established by the EPA.¹² The concentrations of target analytes ranged from 2.65 to 14.6 mg/kg and the spiked

	certified value (mg/kg)	EPA QC criteria (rec.%)	MAE		Soxhlet		Sonication		SFE	
			Recovery (ave.%)	RSD (%,n=3)	Recovery (ave.%)	RSD (%,n=3)	Recovery (ave.%)	RSD (%,n=3)	Recovery (ave.%)	RSD (%,n=3)
<i>Native Compounds</i>										
anthracene	7.3	27-133	69	4.4	46.9	12	46.5	22	55.6	7.5
benzo(a)anthracene	6.5	24-159	101	5.8	122	13	66.7	13	74.5	7.4
benzo(k)fluoranthene	6.5	11-162	101	5.8	122	13	66.7	13	74.5	7.4
benzo(a)pyrene	3.0	17-163	67	6.2	57	4.6	39.4	6.5	53	12
bis(2-ethylhexyl)phthalate	6.9	8-158	118	1.5	118	6.3	170	38	103	7.5
butylbenzy phthalate	3.9	D-152	113	1	113	6	131	26	90.4	6.5
4-chloro-3-methylphenol	5.1	22-147	89.9	0.8	76.9	4.9	73.6	13	86.4	9
4-chlorophenyl phenyl ether	4.8	25-158	96.9	2.8	95.6	7.5	83.4	15	70	7.5
chrysene	2.7	17-168	113	1.9	107	6.7	79.6	14	86.7	6
dibenzofuran	3.8	-	89.6	1.8	88.8	11	76.7	17	63.6	6.3
1,2-dichlorobenzene	8.8	32-129	20.7	5.8	17.6	32	20.4	18	9.9	16
1,4-dichlorobenzene	5.1	20-124	13.3	5.6	10.5	28	14	21	5.9	15
2,4-dichlorophenol	9.1	39-135	69.8	1.1	51.7	15	64.3	26	65.6	9.2
2,4-dichlorotoluene	7.0	39-139	98.6	2.6	80.3	16	67.5	39	72.4	10
2,6-dinitrotoluene	5.2	50-158	95.4	2.3	88.1	8.1	73.7	33	72.1	11
2-methylphenol	12.0	-	50.5	1.3	32.9	15	48.9	18	36.4	11
4-methylphenol	8.7	-	53.9	0.4	42.6	5.5	55.7	21	40.7	15
naphthalene	3.5	21-133	50.2	3.3	44.1	26	49.1	17	33.4	13
n-nitroso-di-n-propylamine	5.4	D-230	68.8	2	73.6	23	74.8	13	55.8	15
pentachlorophenol	15.0	14-176	72.4	3	65.5	3.2	33.5	72	52.1	17
pyrene	6.0	52-115	107	1.1	102	7	141	49	77.5	7.2
1,2,4-trichlorobenzene	2.3	44-142	39.8	4.1	32.9	30	39.8	18	24.4	14
<i>Surrogates</i>										
2,4,6-trinitrophenol	6.5	37-144	89.5	2	41.3	47	67.4	27	82.5	4.5
2-Fluorobipheny	5.0	30-115	77.7	1.2	74.6	14	78.9	10	52.9	14
2-fluorophenol	5.0	25-121	60.4	3.8	50.2	23	62.1	15	49.8	15
nitrobenzene-d5	5.0	23-120	61.7	2.7	54.9	22	66.5	11	41	16
phenol-d5	5.0	24-113	69.4	1.3	65.5	21	73.4	13	57.1	15
terphenyl-d14	5.0	18-137	109	1.9	92.4	20	151	36	77.3	7.6
2,4,6-tribromophenol	5.0	19-122	102	1	51.8	50	64.1	43	80	1.3

Ref: J. of AOAC International 1996, 79, Table 2, 142-156

Ref: J. of AOAC International 1996, 79, Table 2, 142-156

by SFE.¹² The microwave extractions were performed according to the suggested standard operation procedures: a 10-g portion of the spiked soil or standard reference material was extracted by MAE with 30 mL hexane-acetone (1:1) at 115°C for 10 min. Conditions for the extraction by Soxhlet and sonication were performed as described in EPA Method 3540 and 3550, respectively. Six surrogate compounds were added to the respective soil samples immediately prior to extraction. Recoveries were based on ERA-certified values.

concentration for each surrogate was 5 mg/kg.

Overall, the recovery and precision by MAE are better than the other three extraction methods. The recoveries of chlorobenzenes obtained by four methods were low (two dichlorobenzenes $\leq 20\%$, and 1,2,4-trichlorobenzene $< 40\%$). The volatility of these compounds may account for these low recoveries. Recoveries for MAE were 51 to 118% with RSDs of 0.8 to 6.2%; for Soxhlet extraction 33 to 122% with RSDs of 4.6 to 30%; for sonication 34 to 151% except bis(2-ethylhexyl)phthalate with RSDs of 6.5 to

49%; and for SFE 3.4 to 103% with RSDs of 6 to 16%.

The recoveries of 15 basic compounds from NIST 1941a sediment varied widely in all the extraction methods; benzidine was not detected by any of the extraction methods (Table 6). The recoveries of the compounds were 0.7 to 53.6% for MAE; 0.2 to 114% for Soxhlet extraction, 2.4 to 147% for sonication,

concentration for each surrogate is 5000 mg/kg. Although these data were within EPA's acceptance criteria, recoveries by MAE were lower than those achieved for the other technologies. The chromatograms of extracts obtained from MAE were the dirtiest among the three methods, and the SFE extracts were the cleanest. It appears that interference may have contributed to the low recovery of MAE. According to explanation given by authors,

Compound	MAE		Soxhlet		Sonication		SFE	
	Recovery (ave.%)	RSD (% , n=3)	Recovery (ave.%)	RSD (% , n=3)	Recovery (ave.%)	RSD (% , n=3)	Recovery (ave.%)	RSD (% , n=3)
4-aminobiphenyl	2.8	13	24	136	5.5	36	6.6	61
aniline	5.1	59	30	46	40	44	17	18
benzidine	0	-	0	-	0	-	0	-
4-chloroaniline	8.1	40	8.3	79	43	5.8	4.5	120
dibenzo(a)acridine	12	15	58	6.3	60	26	2.4	100
dimethylaminoazobenzene	0	-	0	-	22	23	0	-
3,3'-dichlorobenzidine	44	12	24	56	100	34	62	18
a,a-dimethylphenethylamine	4.1	8.3	9.8	37	2.4	22	5.3	20
1,2-diphenylhydrazine	54	24	114	11	147	21	137	5.3
1-naphthylamine	1	41	0.5	6.9	10	31	6.9	3.1
2-naphthylamine	0.7	9.7	1.7	2.4	2.5	74	2.3	10
2-nitroaniline	51	21	85	12	106	7.9	92	1.7
3-nitroaniline	18	37	4.9	64	58	23	13	8.4
4-nitroaniline	24	20	10	48	75	24	12	63
2-picoline	21	8.8	78	4.1	24	55	20	59

Ref: J. of AOAC International 1996, 79, Table 4,142-156

and 0 to 137% for SFE. Recoveries of these selected basic compounds from freshly spiked soil by microwave heating significantly improved the overall recoveries of MAE to 65 to 102% under comparable extraction conditions, with the exception of benzidine and 2-picoline. These results suggest the matrix effect of the sample may contribute to the low recoveries of MAE. This result is consistent with other studies, which show that the performance of MAE is matrix-dependent.¹²

1.2 PAHs

Table 7 presents the recoveries from a NIST1941 sediment.¹² The reference material contained 14 PAHs with certified concentrations ranging from 361 to 1010 mg/kg in marine sediment. The spiked

the NIST sediment was rich in sulfur and MAE might extract more of this interference from the matrix than the other methods. The recoveries of PAHs by MAE ranged from 42 to 98% with the exception of naphthalene (26%) and Benzo(g,h,j)perylene (37%), and the RSDs ranged from 10 to 33%.

A comparison study for the recoveries of PAHs from a native soil using a 20 min of microwave extraction vs the 6 hr of Soxhlet extraction using the same extraction solvent indicated that the results obtained by the two methods were comparable, 279.8 mg/kg by microwave extraction vs 297.4 mg/kg by Soxhlet extraction.⁹ The RSD is 13% (n = 4) for MAE vs 10% (n=5) for Soxhlet.⁹ However, MAE saves significantly in extraction time and in solvent as compared to Soxhlet extraction.

Table 7. Recovery of Selected PAHs from 1941a Sediment Material										
	certified value (ug/kg)	EPA QC Criteria (rec.%)	MAE		Soxhlet		Sonication		SFE	
			Recovery (ave.%)	RSD (%, n=3)	Recovery (ave.%)	RSD (%, n=3)	Recovery (ave.%)	RSD (%, n=3)	Recovery (ave.%)	RSD (%, n=3)
<i>Native Compounds</i>										
anthracene	184 ± 14	27-133	114	15	112	4.9	114	26	171	40
benzo(a)anthracene	427 ± 25	33-143	79.6	7.3	97.7	3.9	112	30	88.8	7.7
benzo(b)fluoranthene	740 ± 110	24-159	68.2	6.6	137	5.7	131	4.7	128	6.1
benzo(k)fluoranthene	361 ± 18	11-162	68.2	6.6	137	5.7	131	4.7	128	6.1
benzo(g,h,i)perylene	525 ± 67	D-219	51.4	6.9	64.5	2.2	71.3	35	34	9.6
benzo(a)pyrene	628 ± 52	17-163	49.4	6.1	87.2	3.4	83.1	8.6	68.3	3.9
chrysene	380 ± 24	17-168	129	8.6	161	1.4	161	6	159	10
benzo(a,h)anthracene	73.9 ± 9.7	D-227	123	7.2	152	0.9	213	30	128	24
fluoranthene	981 ± 78	26-137	87.7	12	81.4	14	68.4	2.1	62.6	2.6
fluorene	97.3 ± 8.6	59-121	97.9	24	76.7	11	69.7	14	87.4	10
indeno(1,2,3-cd)pyrene	501 ± 72	D-171	57.9	6.5	74.8	4.4	75.1	33	40.8	13
naphthalene	1010 ± 140	21-133	48.5	13	50.3	11	20.6	33	31.7	13
phenanthrene	489 ± 23	54-120	119	28	92.8	3.6	73.5	7	82.4	39
pyrene	811 ± 24	52-115	77.7	13	106	4.5	107	6.3	98.8	4.2
<i>Surrogates</i>										
2-Fluorobipheny	5000	30-115			90.9	4.4	91.6	14	66.5	1.4
2-fluorophenol	5000	25-121			47.6	15	41.7	63	35.5	15
nitrobenzene-d5	5000	23-120			60.9	7.2	50	45	28.6	9.5
phenol-d5	5000	24-113			86.1	6.1	77.1	30	69.4	7.9
terphenyl-d14	5000	18-137			111	6.5	124	16	94.3	6.6
2,4,6-tribromophenol	5000	19-122			82.1	7.6	106	14	81.5	16
Ref: J. of AOAC International 1996, 79, Table 3, 142-156										

Ref: J. of AOAC International 1996, 79, Table 3, 142-156

1.3 Organochlorinated Pesticides (OCPs) and PCBs

Table 8 presents a comparison of MAE with Soxhlet and sonication extractions in the recoveries of OCPs.⁸ Under the established

studies, the extraction recoveries by MAE in general are higher than Soxhlet and sonication extractions, except under specific matrix effects. The average recoveries were 72 to 116% for MAE, 63 to 128% for Soxhlet extraction, and 61 to 108% for sonication. The recovery of hexachlorocyclopentadiene

Table 8. Extractions of Chlorinated Pesticides by Sonication, Soxhlet, and MAE						
Compound	Sonication		Soxhlet		MAE	
	Recovery (ave.%)	RSD (%, n=3)	Recovery (ave.%)	RSD (%, n=3)	Recovery (ave.%)	RSD (%, n=3)
aldrin	66	5.2	78	3.7	87	2.1
a-BHC	70	6.2	70	4.7	94	4.1
delta-BHC	0		68	1.7	97	2.8
4,4'-DDT	108	5.7	128	3.6	116	5.6
dieldrin	79	4.4	96	2.7	86	3.8
endosulfan-I	68	3.9	69	3.3	87	3.1
endosulfan-II	63	5.3	58	8.3	72	6.3
endrin	62	6.4	63	2.7	97	1.9
heptachlor	69	5.2	85	6.7	110	1.4
heptachlor epoxide	61	4.9	70	2.9	95	2.7
hexachlorobenzene	66	5.6	74	7.2	81	1.6
hexachlorocyclopentadiene	45	11	22	96	107	12

Data presented is from Table 2 in Anal.Chem.1995, 67, 2096-2102.

conditions for MAE, the recoveries of these compounds were comparable to those reported earlier for the sonication and Soxhlet extraction techniques. As shown in other

studies, the extraction recoveries by MAE, 107% compared to 45% for sonication and 22% for Soxhlet extraction. The method precision was comparable by using three techniques, with

RSDs mostly within 2 to 6% with the exception of hexachlorocyclopentadiene, which showed a higher %RSD by all three methods.

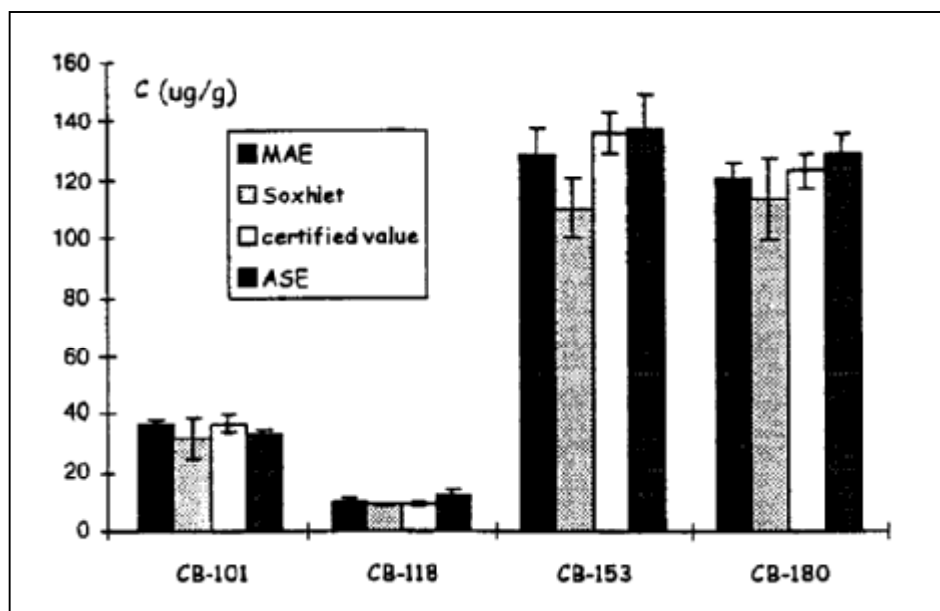
Comparing the performance data on the extraction of 95 compounds listed in EPA method 8270 by various methods under study,¹² MAE and Soxhlet gave the comparable recovery data; sonication gave slightly higher recoveries, and SFE produced the lowest recoveries. MAE gave the best precision, 90 of 94 compounds recovered with RSDs $\leq 10\%$. Soxhlet extraction gave the worst precision, only 52 of 94 compounds recovered with RSDs $\leq 10\%$. The recoveries of polar compounds are generally below EPA acceptable criteria. MRI found that extraction of these compounds by MAE with acetonitrile improved the recoveries of these compounds.¹²

Comparable results in the extraction of PCB isomers by microwave-assisted extraction

with other extraction methods have been reported.⁴⁶ Five aliquots of a certified reference industrial soil containing 4 PCB isomers (CB-101, CB-118, CB-1253 and CB-180) were extracted by Soxhlet, sonication, MAE, and Accelerated Solvent Extraction (ASE). Values obtained from MAE were in good agreement with the certified values (Figure 6). The results of MAE were comparable with ASE and Soxhlet extractions. Both MAE and ASE systems offer high extraction efficiency when operating at their respective optimal conditions. Both extraction procedures significantly reduce extraction time and solvent use, relative to the Soxhlet extraction.

A study using MARS-X microwave extraction system was conducted by the Water Research Institute at the University of Maine to determine the concentrations of chlorinated pesticides and PCBs in fish tissues.⁴² Figure 7 presents comparable pesticide concentrations

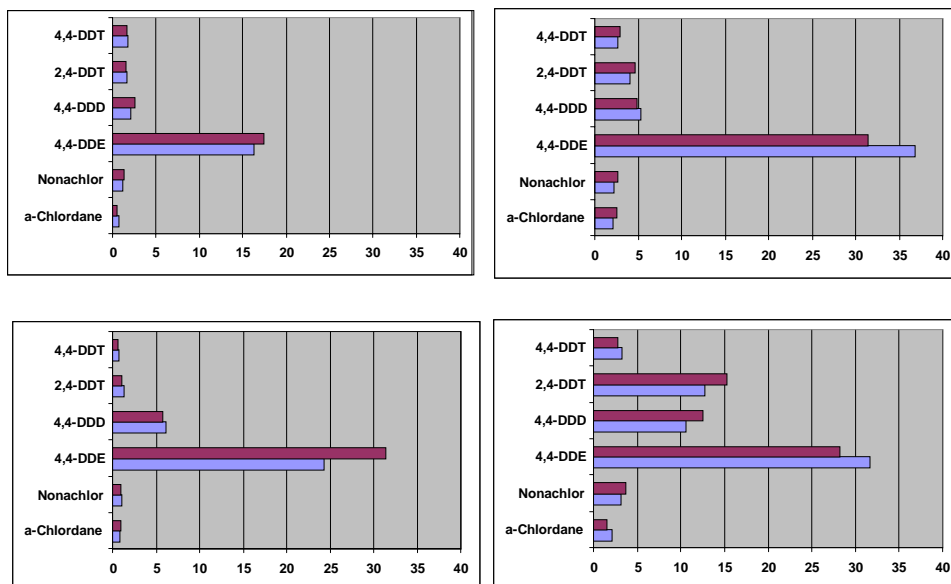
Figure 6. Comparison of Concentrations Obtained by MAE, Soxhlet, and ASE Methods with the Certified Values



Trends in Analytical Chemistry, vol 17, No 10, 1968

Figure 7: Concentrations of Pesticide in Fish (ng/g)

Soxhlet Microwave



Courtesy Water Research Institute, University of Maine

found in various fish tissues using both microwave and Soxhlet extraction methods. Table 9 is the comparison of PCBs results in these fish tissues.

2. Total Petroleum Hydrocarbons

To evaluate the performance of the MES-1000 for the extraction of total petroleum hydrocarbons (TPH), CEM analyzed three soil

samples contaminated with different types of petroleum hydrocarbons in different matrices.⁷ For quality control, duplicate samples and a solvent blank were heated in the microwave apparatus with 30 mL of acetone-hexane (1:1) at 150°C for 15 min. These samples included: (1) a moist soil contaminated with diesel fuel, (2) a dry standard reference material (SRM) containing no. 2 diesel fuel, and (3) soil contaminated with high molecular weight

Table 9. Total PCB Concentrations in Fish Tissues		
Fish Tissue	Concentration (ng/g)	
	Soxhlet	Microwave
Striped Bass 1	8.25	8.86
Striped Bass 2	15.8	16.7
Trout	42.4	53.6
Small Mouth Bass	377	386
White Sucker 1	829	856
White Sucker 2	987	1005
Data are courtesy of Water Research Institute, University of Maine		

hydrocarbons, such as motor oil, transmission fluid, and diesel fuel. These samples were then subjected to extractions by microwave, and the performance was compared to that of Soxhlet and sonication using conditions specified in EPA Methods. For the moist soil, the recovery of diesel-range organics from microwave extraction was comparable to sonication extraction (220 and 250 mg/kg from microwave vs 220 mg/kg for sonication).

For the SRM, the recoveries from microwave extraction and Soxhlet were in good agreement with the certified values (923 and 963 mg/kg for microwave vs certified value of 990 mg/kg), and slightly higher than sonication extraction (758 and 787 mg/kg for sonication). Table 10 shows the TPH recovery from soil contaminated with higher-molecular weight hydrocarbons.⁷

Results obtained from this study demonstrate that recoveries in microwave extractions are comparable to those obtained by standard Soxhlet methods and are more efficient than sonication extractions, specifically for the components of heavier molecular weight of petroleum hydrocarbons. The system has shown to be a viable alternative to extract TPH from highly contaminated soil. On the basis of this performance data, CEM submitted the method for solvent extraction of total petroleum hydrocarbons from solid matrices using closed vessel Microwave heating to ASTM³¹ and was approved.

3. Polychlorinated Dibenzo(p)dioxins and Dibenzofurans (PCDD/PCDF)

Good recoveries for 17 isomers of 2,3,7,8-substituted PCDD and PCDF by microwave extraction were also reported.⁶ Comparable results to those from Soxhlet extraction were obtained from sewage sludge, fly ash, and sediment. Due to the complicated nature of the PCDD /PCDF and their presence at trace levels in the environment, the practical use of MAE for dioxin and related compounds from the above described matrices warrants more studies.

Quality Control and Quality Assurance Program

To ensure that data quality meets project-specific objectives, the user of the Microwave Accelerated Solvent Extraction System should follow the specific guidance established for U.S. EPA SW-846 Method 3500 for sample extractions, and in addition, the guidance for the respective instrumental analytical method.

A method blank should be run concurrently with each batch of analyses to demonstrate that the system and reagents were free from interference. Surrogate compounds should be spiked into the soil matrices prior to sample extraction to monitor the extraction efficiency. Standard Reference Materials containing target analytes should be analyzed to demonstrate accuracy or bias of the extraction method.

Table 10. Total Petroleum Hydrocarbon Recovery from Soil

	Soxhlet (mg/kg)	Sonication (mg/kg)	Microwave (mg/kg)
Solvent	^a Acetone-hexane (1:1)	^b Freon-113	^c acetone-hexane (1:1)
Concentration (mg/kg)	1.33 ± 0.02 (n=6)	0.96, 0.92 (n=2)	1.32 ± 0.01 (n=11)
^a 100mL, 7 hr extraction			
^b 400 mL, 20g sample, modified SW-846 Method 9017			
^c 30 mL extracdton at 150°C, 15 min; 5g sample.			
Ref: American Laboratory, February 1995, Table 6, p.72			

CEM requires that routine instrument maintenance and calibration must be performed every 12 months to assure that performance criteria are met.³⁷ Routine instrument calibration procedures are available to the customers.³⁷ The standard operating procedure (SOP) for instrument performance checks, scheduled calibration checks, and preventive maintenance procedures can be obtained from CEM. CEM indicates that experienced representatives are available to assist customers on technical issues.

Manufacturability

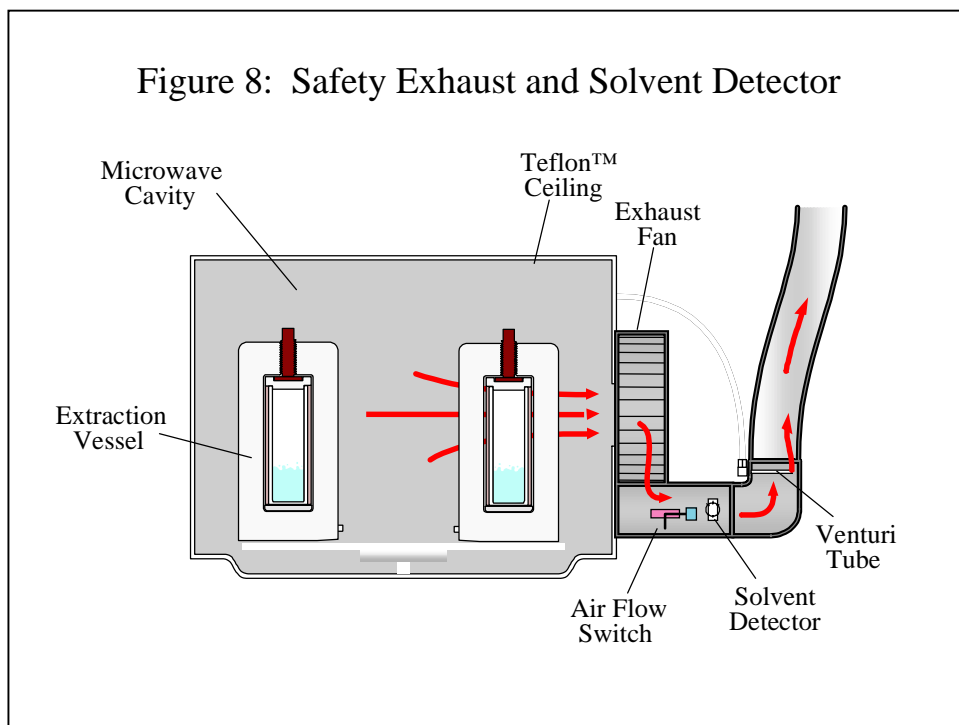
CEM Corp. manufactures and markets instruments within a quality program, which is certified under ISO-9002 by Intertek Testing Services.²⁹ CEM Corporation indicates that its products are designed, developed, and manufactured in conformity with ISO-9002 requirements. Internal and external audits have been performed to maintain ISO-9002 certification. The certification period was recently extended to the February 16 of 2003.^{34, 35} Reports received from all ten users of CEM MES-1000 and MARS-X reflect general consensus that the instrument requires

little maintenance work under normal operating conditions. The instrument downtime is minimal.

Health and Safety

Because many organic solvents are flammable, heating a solvent in a microwave field poses a safety issue. Figure 8 illustrates the schematic of a Microwave System designed for heating organic solvents. The safety features include an exhaust fan to evacuate the cavity air volume approximately once every second.

If the exhaust fan would fail or a blockage would occur downstream of the fan, the airflow switch, located downstream of the exhaust fan, will shut down the system. A solvent detector monitors the cavity for the presence of solvent. The detector shuts down the system if solvent concentrations are 1/10 of the lower explosive limit for a solvent; it will set off an alarm, and post a message for operators. The cavity is coated with PTFE to minimize potential high-energy discharges, and the door is designed to withstand explosion. The user should operate the microwave unit in accordance with CEM's recommended safety instructions.²⁶



1. Worker Safety

Worker safety issues are associated with possible exposure to microwave energy and to solvents. DTSC did not conduct independent tests of CEM's claim that microwave energy exposure is negligible. The maximum allowed leakage at the door is given by CEM as less than 1 milliwatt per square centimeter at the door surface. This is 80% below the maximum level allowed by federal law. The issue of solvent exposure is minimal since the vessels are completely sealed. If the vessels should vent, the instrument has a built-in safety system to detect organic vapors and shut off the system automatically. The MARS-X is part of the "family" of instruments approved under MARS 5 Test Reports. The MARS 5 system has been tested, passed and approved under the Electrical Safety Standards for Laboratory Equipment.³⁹ The testing was conducted by ETL Laboratories, an OSHA Nationally Recognized Testing Laboratory.⁴⁰ The frame designed for GreenChem™ Extraction Vessels provides a unique safety relief mechanism to prevent vessel over-pressurization and rapid cooling after completion of extraction.³³

2. Operator Training Requirements

An important consideration for adoption of this technique is the safety of the equipment for the handling of potentially flammable solvents.³ Common sense and good laboratory practices must be applied to minimize these hazards. Instructions specifically provided by CEM for safe operation are given in the Operation Manual prepared for the Microwave Accelerated Reaction System.²⁶

USERS' SURVEY

The experience of ten users of the CEM Microwave Extraction System was ascertained in a telephone survey conducted during the

period of March 8 to 12, 2000. Among these users, two are the users of Model MES-1000, seven of Model MARS-X, and one is a user of both MES 1000 and MARS-X. The questions posed to the users included the duration of instrument use, the users' applications and satisfaction, reliability of instrument performance, requirements of routine maintenance for the users' specific applications, and the users' perceived advantages or disadvantages of the system relative to other solvent extraction systems. Use of Model MES -1000 varied from 2 to 4 years. Other than the capabilities of temperature control and adequateness of the vessel sealing during high-temperature operation, there was a consensus of satisfaction for Model MES -1000 users. According to CEM, these limitations have been improved in the MARS-X system. Use of Model MARS-X varied from 6 months to one year. Although in service for a shorter period of time, the technology has been shown to be applicable to a variety of matrices, including biological tissues, grains, marine sediments, soils, and fatty foodstuffs. The recoveries in general ranged from 70 to 130%. The analytes included chlorinated pesticides, PAHs, TPH, PCBs, and semivolatile organics. One MARS-X user indicated that the system was good for extraction of nitro-PAHs, because the extraction was completed in a short period in a closed vessel, thus reducing the potential for a photochemical reaction of the compound.

The general comments received from users in this survey are: (1) Saving time, solvent and labor are the major advantages relative to the conventional organic extraction methods such as Soxhlet extraction; (2) The new design of MARS-X expands the cavity to make the operation much easier and provides better temperature control of the operating system; (3) The frame design of MARS-X is much easier to operate than the MES-1000 in which the safety membrane was ruptured easily; (4) The users of MES-1000 and MARS-X, in general, are satisfied with the performance of

instrument for their specific applications; (5) Very little maintenance work is required under normal operating conditions; (6) The instrument downtime is minimal; except in one case; and (7) The CEM staff provides good technical support and is helpful in problem solving and consultation for method development. The users also experienced that the system had been automatically shut down due to leaking solvent under high temperatures. Unlike the MES-1000, the MARS-X has no readout for system pressure.

CEM indicates that the operating pressure is controlled by the temperature and provides no independent function. Pressure readout can be provided, however, as an option upon request.

The vessel can be safely operated at temperatures up to 200°C and their corresponding pressure for all commonly used extracting solvents. Therefore, CEM chooses to make the pressure measuring feature an option. Software will limit the end user from ever programming in a value above 200° C. Vessel safety venting mechanisms will come into play to prevent pressure build up.

SUMMARY OF FINDINGS AND RECOMMENDATIONS

This evaluation report is based on the documents, publications, and method development and research data generated by CEM as well as by MRI as an independent research institute, and by other investigators.

As is the case with many technologies, CEM over time improves its product. Due to the short period of commercialization of the MARS-X solvent extraction system, the validation data for this evaluation were generated mostly by the MES-1000. This report is focussed on the evaluation of solvent extraction system for environmental applications.

Both MES-1000 and MARS-X are based on the same basic operating principle that combines the speed of microwave heating and closed (sealed) vessel technology to achieve

elevated temperatures under controlled conditions. With several new features incorporated in the technology, the MARS-X provides equivalent extraction efficiency, better control of individual vessel temperature, and easier operation without sacrificing performance demonstrated by the MES-1000.

Typically, MAE was operated by extracting 5 to 10 grams of solid sample in 25 to 30 ml of equivalent solvent systems used in the Soxhlet extraction for 20 to 30 min at 110°C to 135°C.

Up to 14 samples can be simultaneously extracted per heating cycle. Results obtained from presented studies consistently indicate that CEM microwave extraction system is capable of achieving an extraction efficiency equivalent to conventional extraction techniques (Soxhlet, sonication and supercritical fluid) for most target analytes listed in the EPA priority pollutants (acid/base and neutral compounds, organochlorine pesticides, PCBs, organophorus pesticides) from various solid environmental media (soil, sediments, and sludge, etc.). In some applications the MAE is better than SFE techniques. Other applications include extraction of TPHs from soil matrices contaminated with various types of petroleum hydrocarbon products and PCBs from various biological tissues.

The results provide little evidence of chemical effects or thermal degradation for most of the environmental pollutants during the extraction process. As with other extraction methods, the recoveries from microwave extraction can vary due to the characteristics of the analyte, the presence of interference in the sample, and the sample matrix. Therefore, it is the responsibility of a user to evaluate independently the factors or interference that are specifically associated with each case of study and to modify the operating parameters as necessary to meet data quality objectives and measurement objectives for the intended application. The quality control procedures for sample extraction specified in U.S. EPA SW-846 Method 3500 should be followed to ensure the defensibility of the data.

Consultation with CEM for special-case applications is highly recommended.

CEM users indicated that the major advantages of CEM MARS-X are significant savings in extraction time, solvent consumption, and labor. The instruments require little maintenance work under normal operating conditions, and instrument downtime is minimal. Microwave extraction has been approved by the U.S. EPA SW-846 Organic Methods Workgroup as Method 3546 for incorporation into SW-846 update IVb for Solid Waste Testing. The CEM Corporation is certified under ISO-9002 by Intertek Testing Services until February 16, 2003. The instrument is tested and approved by ETL Laboratories, a Nationally Recognized Testing Laboratory accredited by OSHA.

On the basis of these findings, this evaluation supports the vendor's claims that technology extraction efficiency of CEM product MARS-X is comparable to the Soxhlet extraction with a reduction in solvent consumption of 80 to 96 % and reduction in extraction times of 95 % on a per-sample basis. The evaluation team recommends certification of the CEM MARS-X microwave accelerated reaction system as an alternative to Soxhlet, sonication, pressurized fluid

extraction and supercritical fluid extraction. It conforms to EPA's pollution prevention goals by reducing the volume of waste solvents.

EVALUATION TEAM AND REPORT AVAILABILITY

The professional team of this evaluation included Ruth R. Chang, Ph.D. (Project Manager), James Cheng, M.S. (Chemistry), Cynthia Dingman, B.S. (QA officer), and G. Wolfgang Fuhs, Dr. sci. nat. (Program manager). The team members acknowledge Dr. Viorica Lopez-Avila at the Mid West Research Institute for her comprehensive and critical review of this evaluation report.

Copies of this evaluation report are available from the Office of Pollution Prevention and Technology Development Division, California Department of Toxic Substances Control, 1001 I Street, P.O. Box 806, Sacramento, CA 95812-0806, or from the project manager.

The certification language is reprinted on the pages that follow. It was published by the California Office of Administrative Law in the California Regulatory Notice Register 2000, Volume 50Z, p. 2136 – 2138, on 15 December 2000.

**CALIFORNIA
ENVIRONMENTAL
PROTECTION AGENCY

DEPARTMENT OF TOXIC
SUBSTANCE CONTROL**

**Final Decision to Certify a Hazardous
Waste Environmental Technology**

The California Environmental Protection Agency, Department of Toxic Substance Control (DTSC) hereby certifies the following company's hazardous waste environmental technology:

CEM Corporation MARS-X Microwave Accelerated Reaction System, a Laboratory Technology for the Extraction of Organic Compounds from Solid Matrices.

Chapter 412, Section 25200.1.5, Health and Safety Code (enacted by Assembly Bill 2060, 1993) authorizes the DTSC to certify the performance of hazardous waste environmental technologies. Hazardous waste environmental technologies are certified pursuant to implementing regulations found in Title 22 of the California Code of Regulations (CCR 22), Chapter 46, Section 68000. Only technologies that are determined not to pose a significant potential hazard to the public health and safety or to the environment when used under specified operating conditions may be certified. Incineration technologies are explicitly excluded from the certification program. The purpose of the certification program is to provide an in-depth, independent review of technologies at the manufacturer's level to facilitate regulatory and end-user acceptance and to promote and foster growth of California's environmental technology industry.

DTSC makes no express or implied warranties as to the performance of the manufacturer's

product or equipment. The end-user is solely responsible for complying with the applicable federal, state and local regulatory requirements. Certification does not limit DTSC's authority to require additional measures for protection of the public health and the environment.

By accepting certification, the manufacturer assumes, for the duration of certification, responsibility for maintaining the quality of the manufactured equipment and materials at a level equal or better than was provided to obtain certification and agrees to be subject to quality monitoring by DTSC as required by the statute under which certification is granted.

DTSC's proposed decision to certify was published in the California Regulatory Notice Register 2000, Volume No. 42-Z, pages 1804-1706 on October 20, 2000 and has been subject to public review and comment. Written comments were not received.

An Evaluation Report supporting the Department's decision is available for review at:

California Environmental Protection Agency
Department of Toxic Substance Control
Office of Pollution Prevention and
Technology Development
P. O. Box 806, 1001 "I" Street, 12th Floor
Sacramento, CA 95812-0806

Or contact:

Dr. Ruth R. Chang, (510) 540-2651,
Hazardous Materials Laboratory
2151 Berkeley Way, Room 515
Berkeley, CA 94704-1011

A description of the technology to be certified, the certification statement, and the certification limitations for the technology of the company listed above follows.

CERTIFICATION PROGRAM (AB 2060) FOR HAZAROUS WASTE ENVIRONMENTAL TECHNOLOGIES

TECHNOLOGY CERTIFICATION

Technology:

MARS-X Microwave Accelerated Reaction System, a Laboratory Technology for the Extraction for Organic Compounds from Solid Matrices

Manufacturer:

CEM Corporation, P. O. Box 200, Matthews, NC 28106, Tel, (704) 821-7015, <http://www.cem.com>

Technology Description

Microwave energy is a non-ionizing radiation that causes heating by migration of ions and rotation of molecules with dipole moments, but does not cause changes in molecular structure. During the sample extraction process, dipole rotation refers to the alignment of polar solvent-sample molecules due to exposure to the electric component of the microwave field. As the electric field decreases, induced disorder is restored which results in thermal energy being released. The technology combines the speed of microwave heating and closed (sealed) vessel technology to achieve elevated temperatures under controlled conditions. When sample-solvent mixtures are exposed to microwave energy at temperatures above the atmospheric boiling point of solvent, the analyte desorption rate from the sample is significantly increased. The combined effect of high temperature and rapid heating of the extraction solvent in a closed-vessel system increases the extraction efficiency and significantly reduces the extraction time. The system is equipped with an inboard pressure and a temperature control system for regulating sample extraction

conditions via magnetron power output control. The Microwave Accelerated Reaction System (MARS-X) is a closed-vessel heating system designed for laboratory use in extracting a wide range of organic materials from solid matrices. The system can be used for the microwave-assisted process without replacing a non-polar solvent with a polar or co-solvent system. The MARS-X can process 14 samples simultaneously; typical extraction times are 15 to 20 minutes per heating cycle. Samples are limited to a maximum size of 20 grams. Solvent systems commonly used in Soxhlet extraction are applicable for the MARS-X system. Solvent volumes are in general 25 to 30 mL per sample. The maximum operating conditions for the system are 200° C and 200 psi from GreenChem™ and 140 psi from CleanChem™ with typical operating conditions at 110 – 135° C and 100 psi.

Certification Statement

Under the authority of Section 25200.1.5 of the California Health and Safety Code, the Department hereby certifies the MARS-X Microwave Accelerated Reaction System manufactured by CEM Corp. Matthews, NC 28106, as a Laboratory Technology for the extraction of semivolatile organic compounds for PAHs, organophosphorus pesticides, organochlorine pesticides, polychlorinated biphenyls, acid, base and neutral compounds and petroleum hydrocarbons in soil, sediments, and sludges.

According to the instrument operating conditions suggested by the manufacturer, the CEM microwave extraction system is capable of achieving an extraction efficiency equivalent to conventional extraction techniques for most target analytes listed as EPA priority pollutants from various solid matrices. There is little evidence of chemical effects or thermo-degradation for most environmental pollutants during the extraction process. The recoveries of microwave extraction can vary due to the properties of the

analyte, the presence of interferences, and matrix factors. Consultation with CEM for special-case applications is recommended.

The MARS-X is equipped with safety features to monitor the cavity for the presence of solvent. The detector shuts the system off automatically, if the solvent concentration reaches 1/10 of its lower explosive limit. An alarm will sound and post a message for operators. The operator should operate the microwave unit in accordance with the safety recommendations by CEM.

Limitations of Certification

The Department makes no express or implied warranties as to the performance of the manufacturer's product or equipment. The Department has not conducted any bench or field tests to confirm the manufacturer's performance data. Nor does the Department warrant that the manufacturer's product or equipment is free from any defects in workmanship or material caused by negligence, misuse, accident, or other causes.

The Department believes, however, that the manufacturer's product or equipment can achieve performance levels set out in this Certification. Said belief is based on a review of the data submitted by the manufacturer and other information, and is based on the use of the product in accordance with the manufacturer's specifications.

This certification is subject to the regulations found in Title 22 of the California Code of Regulations (CCR22), Chapter 46, Section 68000, which include the duration of the Certification, the continued monitoring and oversight requirements, and the procedures for certification amendments and decertification.

By accepting this Certification, the manufacturer assumes for the duration of the Certification, responsibility for maintaining the quality of the manufactured materials and equipment at a level equal or better than was

provided to obtain this Certification and agrees to be subject to quality monitoring by the Department as required by the law under which this Certification is granted.

Specific Conditions

CEM shall follow their established quality control and quality assurance program to ensure that the materials used in manufacturing and the quality of the instrument meets standards certified under ISO-9002.

CEM shall maintain their standards for ensuring that users receive applicable training in operation and maintenance of the technology. The quality control procedures for sample extraction specified in U.S. EPA SW-846 Method 3500 must be followed to ensure meeting the project specific requirements. A method blank and surrogate compounds must be included in the operation to validate the instrument performance.

Through updates of user guides, the Manufacturer shall inform the user of interferences and matrix effects that potentially affect the performance of the system, as they become known to the Manufacturer.

Users shall follow the manufacturer's instructions for installation, operation, and maintenance. Users shall develop and follow a plan in accordance with their facility's quality management system for validating the system at appropriate intervals according to the guidance set for the MARS-X system.

Basis for Certification

The certification of this technology is proposed on the basis of the information and data packages pertaining to the performance of MES-1000 (an initial Model of closed-vessel microwave solvent extraction system) and MARS-X submitted by the CEM. These performance data substantiate the following

findings: (1) The technology extraction efficiency of the CEM MARS-X is comparable to Soxhlet extraction; (2) The technology provides environmental and economic benefits over the conventional solvent extraction methods; (3) The instrument is tested and approved per OSHA guidelines; (4) The company is certified under ISO-9002 standards; and (5) Satisfactory reports were received from user's survey for the MES-1000 and MARS-X closed-vessel microwave extraction systems and service provided by the company. A listing of the documentation available for this evaluation is contained in the Evaluation Report.

Recommended Applications

The CEM MARS-X microwave accelerated solvent extraction system is intended for the extraction of organic compounds from environmental samples in the laboratory for subsequent analysis using appropriate analytical methods. Applications include extraction of semivolatile organic compounds, including PAHs, chlorinated pesticides, PCBs, organophosphorus pesticides, acid, base, and neutral compounds and total petroleum hydrocarbons from soil, sediments and sludge. The microwave extraction operating in according with conditions established by the manufacturer can serve as a viable alternative for conventional solvent extraction methods.

With the advantages of substantial reduction in the sample extraction time and solvent

consumption, the MARS-X technology significantly improves the sample turnaround time for data generation for the protection of public health and the environment.

Regulatory Implications

DTSC's certification does not change the regulatory status of the extraction of organic compounds from solid matrices; it is intended, however, to facilitate and encourage the acceptance of this technology where a project's data quality objectives can be met by its use. To this end, regulatory programs are encouraged to consider the Department's findings regarding this technology, depending on each program's objectives and constraints. State-regulated facilities may contact state permitting officers regarding the use of the technology for sample preparation for organic compounds. Other local and state government permitting authorities may take this certification under consideration when making their permitting decisions. Project managers may consider using this technology where its use can contribute to the project and its data quality objectives.

Duration of Certification

This certification takes effect 30 days after the date of publication of this Notice. Unless amended or revoked for cause, this certification will remain in effect for three years.